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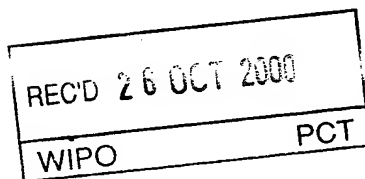
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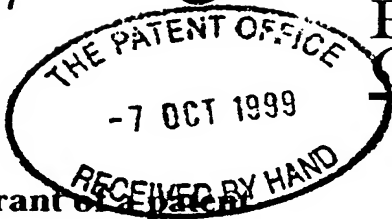
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1. Your reference CJH01467GB

2. Patent application number **9923747.1**
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4. Title of the invention COMPOSITE MATERIALS, THEIR PRODUCTION AND USES

5. Name of your agent (if you have one) Gill Jennings & Every

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Patents ADP number (if you know it)

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Description 21

Claim(s) 3

Abstract 1

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11. For the applicant
Gill Jennings & Every

I/We request the grant of a patent on the basis of this application.

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7 OCTOBER 1999

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COMPOSITE MATERIALS, THEIR PRODUCTION AND USESField of the Invention

The present invention relates to a process for
5 producing a composite of integrated, polymerised, inorganic
and organic polymer networks. It also relates to the
composite material itself, and to its use in applications
where its hardness, excellent optical properties and low-
temperature curing can be exploited beneficially.

10 Background of the Invention

Polymer-based materials are routinely used as
alternatives to glass in many situations where the weight,
tendency to shatter, or expense of glass contraindicates
its use. In turn, polymeric materials such as acrylic
15 polycarbonates have inherent drawbacks, particularly with
regard to poor abrasion-resistance, but also with regard to
poor resistance to degradation by UV light, and poor
corrosion resistance on exposure to organic solvents.

In order to address these problems, protective
20 coatings have been applied on to polymeric materials.
Silica-based materials have been widely used for this
purpose, typically made by colloidal sol-gel techniques, in
which silica particles coalesce and ultimately gel to form
an extensive silica network. However, these materials offer
25 only limited protection. Furthermore, due to the inert
nature of these materials, and in particular their low
levels of cross-linking, there is little scope for further
improvement in either their performance or their
versatility.

30 Coatings provided by way of polymeric sol-gel
techniques have higher levels of cross-linking, and
therefore significantly better mechanical and chemical
resistance than the conventional silica-based materials.
Typically, in polymeric sol-gel techniques precursor
35 molecules, such as alkoxides, are hydrolysed in a mixture
of water and solvent, and proceed to undergo a transition
from a sol to a gel state by polycondensation.

Unfortunately, however, removal of the solvent after gelation, by forced drying or by natural evaporation, introduces stresses within the gel structure, which at coating thicknesses greater than around 1.5 μm tends to
5 result in cracking, and a loss in performance. One approach to coping with this restriction is to apply multiple thin coatings, usually with a practical limit of 20 to 30 coats. However, this is cumbersome, and increases production costs, and also results in relatively rigid
10 coatings.

Where coatings thicker than 1.5 μm are needed composite inorganic/organic materials have been employed. These materials are typically prepared by incorporating a polymerisable organic component into a colloidal sol-gel
15 system, and are generically termed ORMOCERS® (Organically-Modified Ceramics). ORMOCERS can be thought of as comprising a network of agglomerated silica particles within an organic polymer network. There is little interpenetration between the two networks.

20 While materials of this type form relatively hard, abrasion-resistant coatings, at silica loadings of around 25% by weight and above, where optimum hardness is achieved, transparency problems have been encountered. Furthermore, until relatively recently most of these
25 materials have tended to cure at temperatures of around 200°C, or higher, rendering them unsuitable for application to substrates having low softening points, e.g. thermoplastic substrates having softening points of 150°C or lower.

30 The development of low temperature coating materials which do not suffer from the draw-backs of the hitherto used silica-based materials is, therefore, very much in demand.

Furthermore, the protective materials known in the art
35 tend to be applied as coatings since they lack the strength and optical properties to be used in their own right as replacements for glass. However, coating one material onto

another, typically different, material is far from ideal. Not only is it cumbersome, but poor affinity between the coating material and the substrate to be coated can be troublesome, leading in certain instances to the coating
5 peeling away from the substrate. It would therefore be very desirable to dispense with the need to apply separate, protective coatings to polymeric substrates.

Accordingly, the development of materials which can be used as coatings and which can also be cast and moulded, or
10 otherwise shaped, into relatively large monolithic structures would be welcomed.

Summary of the Invention

According to a first aspect of the present invention, a process for producing a composite material comprises the
15 steps of:

(1) initiating polymerisation of inorganic monomers, to form a sol;

(2) forming an homogeneous mixture comprising the sol and organic monomers; and

20 (3) polymerising the organic monomers and taking polymerisation of the inorganic monomers substantially to completion, to form a composite material comprising a mixture of an inorganic polymer and an organic polymer.

According to a second aspect of the present invention,
25 a novel composite material is obtainable by the process outlined above.

The composite material of the present invention embodies a more intimate mixture of inorganic and organic components than has been achieved in the prior art. The
30 high levels of transparency that can be achieved supports interpenetration of the inorganic and organic polymer networks on the nanometre scale. It is believed that this level of intimacy of mixing of inorganic and organic components may be responsible for the excellent performance
35 properties of the composite material of the present invention.

The composite material has excellent abrasion resistance, hardness and flexibility, and lacks the tendency to crack. It can, therefore, be formed into monolithic structures. The composite material may be formulated to be transparent, and indeed this is where the primary interest lies. Although the composite material may be formulated to be opaque according to its desired application, by selecting an appropriate organic component, and/or including additives, e.g. pigments. Furthermore, the composite material may be formulated to cure at relatively low temperature, rendering it suitable for coating polymeric materials having relatively low melting points or softening temperatures.

According to further aspects of the present invention, the composite material finds use in a variety of applications, as defined in the claims, and as described in detail hereinafter.

Description of the Invention

The process of the present invention is a modified polymeric sol-gel process. An important aspect of the process, and in particular to achieve the desired interpenetration of inorganic and organic polymer networks, is the formation of an homogeneous liquid mixture of inorganic and organic monomers prior to substantial completion of the inorganic polycondensation reaction to form an inorganic polymer, or gel. In the context of this Application, an homogeneous mixture is one which, when observed by the human eye, is essentially uniform and not partitioned in two separate phases.

Typically, polymerisation of the inorganic monomers is initiated by hydrolysis of hydrolysable monomer precursors, and subsequent polycondensation of the resulting monomers. Accordingly, the invention will be described primarily with this in mind. However, polymerisation of the inorganic monomers may be initiated by other means, for instance starting from monomer precursors which are activated to polymerisable form by means other than hydrolysis, for

instance by another chemical reaction or by heat or electromagnetic radiation. Irrespective of the type of inorganic monomers, or inorganic monomer precursors, used in the process of the invention, similar considerations to those described below will apply.

In the context of the present Application, by an "hydrolysable inorganic monomer precursor", we mean any inorganic molecule which is activated by hydrolysis to a polymerisable inorganic monomer, which, on polycondensation with similar hydrolysed monomers, forms a sol (inorganic oligomers or colloidal solution), and ultimately an inorganic polymer or gel. The precursor must, therefore, include at least one hydrolysable bond. The term "inorganic" is used in this context to denote the presence in the precursor molecule of an inorganic element, typically one giving rise to a ceramic material, e.g. silicon or aluminium, or a metal, e.g. titanium, zirconium, yttrium, and other transition metals.

The inorganic monomer precursors for use in the present invention may be any of those conventionally used in polymeric sol-gel techniques. Examples of suitable inorganic monomer precursors include alkoxides, substituted alkoxides, having one or more non-hydrolysable ligands, e.g. alkyl-substituted alkoxides, nitrates, acetates, and mixtures thereof. The preferred inorganic monomer precursors are alkoxides, and the most preferred are alkoxysilanes, particularly the tetra-alkoxysilanes in which each alkoxy group has 1 to 10 carbon atoms. Particularly beneficial results are obtained when a mixture of unsubstituted and substituted alkoxides is used. Suitable substituted alkoxides include vinyltriethoxysilane (VTEOS), 3-(trimethoxysilyl)propyl methacrylate (MPTMA) and 3-(glycidyoxypropyltrimethoxysilane) (GPTS).

In order to hydrolyse the inorganic monomer precursors, water is either added to the inorganic monomer precursors, or is synthesised *in situ*. Typically, hydrolysis of the inorganic monomer precursors is achieved

by formation of an homogeneous mixture with water and, optionally, an organic solvent. Alternatively, the precursors may be dissolved in an organic solvent and water added to the resulting solution in a controlled manner, as is conventional in sol-gel techniques, to avoid development of clumps of partially-hydrolysed molecules. Suitable organic solvents include any of those conventionally used in polymeric sol-gel techniques. Typically, the solvent will be a low boiling point organic liquid, for instance having a boiling point lower than 100°C, and will usually be an alcohol.

The solvent acts to improve the miscibility or compatibility of the inorganic and organic monomers. An alternative to using a solvent would be to use a liquid which is not a solvent for the inorganic or organic monomers, and include within the system one or more materials to improve the miscibility of the different types of monomer. Examples of such materials include, but are not limited to, anionic, cationic and non-ionic surfactants, and fluorine-containing surfactants. With selection of an appropriate material, it may be possible to avoid the use of organic solvents altogether, and simply use water to suspend the inorganic and organic monomers. This would be particularly desirable in view of current environmental pressures on industry to reduce emissions of volatile organic compounds (VOC's).

If, as is less preferred, water is to be synthesised *in situ* in the reaction mixture, this can be achieved, for example, by including an alcohol in the reaction mixture and then adding a weak acid, for example acetic acid, again in a controlled manner.

It may be necessary to use a catalyst to initiate hydrolysis of the inorganic monomer precursors. Suitable catalysts include any of those conventionally used in polymeric sol-gel techniques, for instance mineral acids such as hydrochloric acid and nitric acid and bases such as sodium hydroxide and ammonia. Alternatively, depending

upon the nature of the inorganic monomer precursors, hydrolysis may proceed spontaneously.

The amount of water used in the process of the invention should generally be sufficient to hydrolyse all the inorganic monomer precursors, and will, therefore, depend upon the nature of those precursors, and in particular the number of hydrolysable bonds that they contain. Because water is produced during the polycondensation reaction, it will be not normally be required to use a 1:1 water:hydrolysable bond molar ratio, although such ratios may be used if desired. Typically, however, the molar ratio of water:hydrolysable bonds will be less than 1:1, down to around 0.5:1, or slightly higher than 0.5:1 to compensate for diffusion effects. For instance, where the inorganic monomer precursors are tetraalkoxysilanes, having four hydrolysable bonds, preferably the molar ratio of water:hydrolysable bonds will approach 2:4, such that the molar ratio of water:tetraalkoxysilanes will approach 2:1. As mentioned above, higher amounts of water may be used, but as unreacted water must be removed prior to formation of the final composite, this is less preferred.

After initiation of hydrolysis of the inorganic monomer precursors, inorganic polymerisation proceeds spontaneously, typically over extended periods of time e.g. up to several months or significantly longer, for instance for a few years. The sol ages, and ultimately, when inorganic polymerisation is substantially complete, forms a gel or inorganic polymer. The ageing process may, if desired, be catalysed by addition of a small quantity of mineral acid, and may be accelerated by raising the temperature to more than 25°C, typically to within the range 30°C to 100°C. Higher temperature may be used, but may be limited by the nature of the organic monomer, and/or, if the composite is to be used as a coating, the nature of the substrate to be coated.

In some cases, however, slow polymerisation may be preferred, for instance to enhance the shelf-life of the product. This is particularly important in the context of coatings, which must remain relatively fluid for application to a substrate. Then, on application to the substrate, both inorganic and organic polymerisation may be taken substantially to completion.

The process of the present invention requires formation of an homogeneous mixture comprising an inorganic sol and organic monomers. According to one embodiment of the present invention, the organic monomers are mixed with the inorganic monomer precursors prior to initiating hydrolysis, or other activation, of those precursors to form a sol. In this case, however, the organic monomers should be water-tolerant, and in particular polymerisation of those organic monomers should not be initiated until after formation of an inorganic sol.

According to another, preferred, embodiment of the present invention, the organic monomers are only added after initiating hydrolysis, or other activation, of the inorganic monomer precursors, when at least an initial sol has been formed. In other words, the inorganic and organic monomers are simply mixed together, although some unhydrolyzed, or unactivated, inorganic monomer precursors will still be present. Preferably, the sol is allowed to age, for instance by leaving to stand, or by exposing to elevated temperature, prior to addition of the organic monomers. However, it is essential that the sol remains liquid on addition of the organic monomers in order to allow homogeneous mixing of the inorganic and organic monomers, which is essential to achieve interpenetration of the inorganic and organic polymer networks in the final composite material.

The degree of ageing of the sol prior to addition of the organic monomers affects the properties of the resulting composite material. For instance, if, as is preferred, the organic monomers are not added to the sol

until hydrolysis of the inorganic monomer precursors is substantially complete, the resulting composite material will take on more of the properties of the inorganic polymer than the organic polymer. The final properties will
5 however also be determined by the loading level of the inorganic monomer. Completion of hydrolysis of the inorganic monomer precursors may be determined, for instance, by any technique capable of detecting the presence of free water in the system, for example NMR,
10 FTIR, etc.

Typically, the sol will be allowed to age for several hours before adding the organic monomers, e.g. for at least twelve hours, or for a day or several days, depending upon the properties required in the resulting composite
15 material. However, as inorganic polymerisation may continue for months, or even years, the sol can be allowed to age for considerably longer periods of time. Ageing of the sol may be achieved, or accelerated, by heating, typically to a temperature of 30° to 100°C, as mentioned
20 above.

As mentioned above, in order to achieve the desired intimate level of mixing of inorganic and organic polymer networks in the final composite, it is necessary that the inorganic and organic monomers are homogeneously mixed
25 prior to formation of the final inorganic polymer, or gel. Accordingly, the organic monomers used in the present invention are either liquid at room temperature, approximately 25°C, or they are solid organic monomers dissolved in an organic solvent which is compatible with
30 the overall sol-gel process.

The nature of the organic monomers is selected according to the properties required in the final composite material. Typically, the organic monomers will be selected to provide strength and abrasion-resistance and, where
35 desired, transparency. Preferably, the organic monomers used are those which, upon polymerisation, form thermoplastic or thermosetting polymers, preferably

thermoplastic polymers. Examples of suitable monomers include carbonates, (meth)acrylates, terephthalates, urethanes, and mixtures thereof. Organometallic monomers may also be used, but in this case they will not contain
5 hydrolysable bonds.

Preferably, the organic monomers polymerise at relatively low temperature, e.g. lower than 150°C, after addition of a suitable initiator, or by irradiation, e.g. with UV or IR light, or bombardment with X-rays or electron
10 beams, so as to be applicable as coatings for thermoplastic or thermosetting materials having low melting points. Monomers which give rise to polymers which have good resistance to organic solvents are also preferred. In the case of the carbonates, therefore, aliphatic carbonates as
15 opposed to aromatic carbonates are preferred.

Depending upon the nature of the inorganic monomers and the organic monomers it may be desirable to include further organic solvent prior to substantial inorganic polymerisation, so as to enhance miscibility of the
20 inorganic and organic components. Surprisingly, subsequent removal of this solvent, together with other volatile components, e.g. those produced in the polycondensation reaction, does not result in deleterious effects in the final product, i.e. cracking.

25 Typically, organic polymerisation is initiated before inorganic polymerisation is substantially complete and a gel has been formed. In some cases, however, it may be desirable to delay organic polymerisation until after formation of a gel.

30 Polymerisation of the organic monomers may be initiated in any conventional manner, which will be determined by the nature of the organic monomers. It will normally involve the use of a polymerisation initiator. If a chemical polymerisation initiator is used, preferably
35 this is added only after substantial inorganic polymerisation has occurred, so as to prevent premature organic polymerisation, prior to formation of an inorganic

gel network. Otherwise, the polymerisation initiator should be added in an inactive state, for activation only when substantial inorganic polymerisation has occurred.

Other, preferred, options are to employ organic monomers which are radiation-curable, for instance UV- or IR-curable monomers, or monomers curable by bombardment with electron beams or X-rays, or which cure on heat treatment. Examples of UV-curable monomers include urethanes and acrylates.

In the case of coating materials, organic polymerisation is usually delayed until after coating on to a substrate. Therefore, if heat is used to initiate or accelerate organic polymerisation, the temperature should be selected so as not to have any deleterious effect on the substrate to which the coating is to be applied. In the case of thermoplastic or thermosetting substrates, relatively low temperatures should be used, typically lower than 150°C, and more typically in the range 30 to 80°C.

If desired, a protective cover sheet may be used to exclude oxygen which may interfere with the organic polymerisation reaction.

To improve the shelf-life of coating materials it is generally preferred to delay substantial organic polymerisation until after coating on a substrate. In the case of a chemical initiator, this may mean delaying addition of this until just prior to, or possibly during, the coating operation.

Prior to completion of inorganic polymerisation, preferably at least some solvent, and more preferably substantially all solvent is removed, together with any volatile components produced during the hydrolysis and polycondensation reactions. By volatile components typically we mean components boiling at lower than 100°C, including water and other polar or protic solvents. Removal of solvent is important to avoid potential separation of the inorganic and organic components in the final composite material. Conventional methods for the

removal of solvent, including any other volatile components, may be employed, e.g. evaporation techniques.

Solvent removal may take place in a number of steps. For instance, some solvent may be removed after ageing of the inorganic sol and prior to addition of the organic monomers, and/or solvent may be removed prior to initiating organic polymerisation and/or formation of the final composite material.

Solvent removal tends to be more important in the preparation of bulk samples, or stand-alone articles, e.g. having thicknesses of above about 1mm, than for coating materials. This is because once polymerisation of a bulk sample is complete, any solvent trapped therein is very difficult to remove. Coatings, however, have a higher surface area to volume ratio than bulk samples, allowing solvent and any other volatile components to "flash-off" during curing at elevated temperature.

In the case of bulk samples it is particularly preferred that the reaction mixture is substantially free of solvent and other volatile components just prior to the onset of organic polymerisation. In practice, this means that the reaction mixture should preferably contain less than 10% by weight of solvent and/or other volatile components when organic polymerisation is initiated, more preferably less than 5% by weight.

The relative proportions of inorganic monomer precursors and organic monomers used in the process of the invention are selected according to the properties desired in the final composite material. Typically, the amount of organic monomers used will be in the range from 5% to 95%, preferably 15% to 85%, more preferably 25 to 75%, by weight based upon the total amount of inorganic and organic monomers present prior to inorganic polymerisation. For instance, when hardness is the primary aim, the composite material will typically comprise at least about 50% by weight of inorganic material. Where, however, flexibility with good hardness is the primary aim, or other properties

typically associated with the organic polymer component of a composite material, the organic polymer should be present in an amount of greater than about 50% by weight, and typically at least about 60% by weight.

5 The proportions of the inorganic monomer precursors and organic monomers necessary to give rise to a particular inorganic, or organic, loading can be calculated relatively simply from a knowledge of the reactions taking place in the sol-gel process. For instance, for any desired
10 inorganic loading level, the oxide content of the sol is first calculated, excluding any contribution from alcohols produced during the course of the polycondensation reaction. In other words, it is necessary to calculate the oxide content of the sol which will potentially solidify to
15 form the inorganic polymer. The amount of organic monomers used in the process can then be adjusted according to the proportion required in the final composite material.

 In order to enhance further mixing of the inorganic and organic polymers it is preferred to include in the
20 process of the present invention a reagent capable of cross-linking, or otherwise engaging, the inorganic and organic polymer networks in the final composite material. Suitable cross-linking agents may be difunctional or multifunctional in nature, giving rise to 3D-networks. The
25 nature of the cross-linking agent will depend upon the nature of the inorganic and organic monomers. For instance, when the inorganic monomer precursors comprise an alkoxide, a preferred cross-linking agent is an alkoxide substituted with a non-hydrolysable organic group, such as
30 an alkyl-substituted alkoxide. Materials of this type have conventionally been used in the production of ORMOCERS®, and specific examples are given above. As mentioned above, alkyl-substituted alkoxides may also be used as the inorganic monomers precursors. When used as cross-linking
35 agents, however, the alkyl-substituted alkoxides are typically mixed with the inorganic monomer precursors, or

the resulting sol in amounts in the range 0.01 to 1.0 mole per mole monomer.

The properties of the composite material of the present invention may further be adjusted according to its desired application, through the use of additives conventional in the art. For example, fluorine-containing reagents may be added to the composite material to improve its hydrophobicity. Alternatively, reagents may be added to confer hydrophillic characteristics. Dyes and pigments may be added for tinting, for example to prepare paints. UV-screening compounds may be incorporated into windscreens and spectacle lenses for eye-protection, or into coatings for substrates susceptible to UV degradation. Photochromic and electrochromic compounds may be incorporated into the composite material, for instance when it is to be used for reactalite lenses or to provide other visual effects.

Furthermore, the hardness of the composite material of the present invention may be increased by adding other ceramic materials, for instance those conventionally used as fillers, such as silica, silicon carbide, and alumina. Generally, however, such ceramic materials have particle diameters greater than 300 to 400 nm, and will therefore interfere with visible light transmission by the composite material, resulting in a loss in transparency. Composite materials modified in this manner may therefore be valued more for properties such as hardness, solvent resistance and adhesive strengths than for their transparency.

The composite material of the present invention may be used as a coating for a wide variety of substrates. As the composite material may be formulated to have a relatively low polymerising, or curing, temperature it is particularly suitable for coating polymeric materials having relatively low melting points, for example of 150°C or lower. Examples of such polymeric materials include thermoplastic and thermosetting materials such as polycarbonates, polesters such as polyacrylates and polyterephthalates, and polyurethanes. The enhanced scratch/abrasion resistance

imparted to these materials by way of coating with the composite material of the present invention will allow them to be considerably more widely utilised than they are at present.

5 The composite material may be coated on to a substrate by any conventional means, for example dipping, spraying, roll coating or brushing. For practical purposes, and as mentioned above, it is preferred to apply the composite material to a substrate prior to completion of
10 polymerisation of the inorganic and organic monomers. Otherwise, the composite material may be too rigid to apply evenly. In fact, it is most preferred to apply the composite material to a substrate prior to start of polymerisation of the organic monomers. Accordingly, a
15 further aspect of the present invention comprises a composition comprising an inorganic sol obtainable by hydrolysis of hydrolysable inorganic monomer precursors, and, mixed therewith, organic monomers.

Due to its high internal strength, the composite
20 material may be applied at relatively high coating thicknesses, for instance up to 1 mm, or higher, but generally it will be applied at a coating thickness of up to 100 μm , typically 5 to 100 μm .

Ideally, the composite material is selected to be
25 compatible with the substrate that it is to coat. However, in this case, care should be taken that the polymerisation initiator system used does not cause degradation of the substrate itself. Furthermore, depending on the nature of the inorganic monomer used, and in particular if these are
30 alkoxysilanes as is preferred, it is not necessary to apply a primer to the substrate prior to coating.

As an alternative to coating, the composite material of the present invention may be cast, shaped or moulded in a similar manner to glass and known thermoplastic and
35 thermosetting polymeric materials. It may also be extruded.

The composite material of the present invention, therefore, potentially has a very wide variety of applications. In particular, when the composite material is transparent it may be used as a direct substitute for glass, or hitherto known glass substitutes. For example, the composite material may be used in building or vehicle, windows, windscreens e.g. for automobile and aircraft, spectacle lenses, camera lenses, protective visors, optical filters and light casings, since the composite material can be adapted to perform effectively in all these specialised and demanding contexts. Therefore, it is envisaged that through use of the composite material of the present invention it may be possible to eliminate the need to apply abrasion-resistant coatings to transparent articles in many cases, thereby providing significant benefits in terms of reducing production costs and improving convenience of manufacture.

In addition to its use as a coating, and as a substitute in its own right for glass, the composite material of the present invention may also be employed as an adhesive, or bonding agent, or a sealant, particularly for polymeric materials, especially plastics, which do not normally adhere very well to each other, but also glasses, other ceramics, and metals. This is because the composite material of the present invention tends to have high affinity to a wide variety of substrates.

When it is to be used as an adhesive or sealant, typically a precursor to the composite material of the present invention, which is at an intermediate stage of polymerisation, will be coated on to one or more of the surfaces to be bonded or sealed together, and the surfaces to be bonded will then be brought into contact with one another. Then, on completion of polymerisation, a secure bond is formed. The composite material of the present invention is particularly suited for use as an adhesive when polymerisation of the inorganic and organic components takes place relatively quickly, resulting in a fast-setting

adhesive layer. One could also envisage the present invention in the form of a two-component adhesive, one component comprising an inorganic sol and the other organic monomers, for intimate mixing, then curing, or
5 polymerisation.

The composite material may also be used as an insulator in multilayer printed circuit boards. Materials of this type may be formulated to have relatively uniform coefficients of thermal expansion (CTE's) in at least the
10 x- and y-planes, leading to improved registration accuracy in the formation of multilayer circuit boards.

The following examples further illustrate the present invention.

Example 1

15 A sol was prepared as follows:

Component A: 41.7 g triethoxysilane (TEOS) was placed in a beaker, and an intimate mixture of 36.8 g methanol and 7.21 g water was added thereto.

Component B: 30.0 g 3-trimethoxysilyl(propylmeth-
20 acrylate) MTPMA was placed in a beaker, and an intimate mixture of 22.2 g methanol and 3.26 g water was added thereto.

Components A and B were then stirred, separately, in sealed beakers for about 30 minutes, after which they were
25 combined, and stirred for about 30 minutes, again in a sealed beaker.

The resulting sol was then aged by heating at 80°C for about 24 hours to promote formation of the inorganic network. 100 g of the aged sol was then mixed with 28.3 g
30 of UV-curable aliphatic urethane acrylate monomer sold by Akcros Chemicals under product code 210TP30, and 1.4 g of Irgacure® 500 (supplied by CIBA Speciality Chemicals) as polymerisation initiator. The resulting mixture was then subjected to evaporation to remove any residual methanol,
35 any alcohol produced during the polycondensation reaction, and residual volatiles.

The liquid remaining after evaporation was then coated on to an acrylic substrate at a thickness of 50 μm . The coated substrate was then heated at 40°C for one hour in an air oven, to enhance formation of the inorganic polymer network. The coated substrate was then irradiated for five minutes under a UV light having a power rating of 43.6 mW/cm², to cure the organic monomer and yield the final composite material. This composite material had a 50% by weight ceramic loading, by virtue of the proportions of the inorganic monomer and organic monomer utilised in its preparation.

Examples 2 and 3

Example 1 is repeated adjusting the amount of organic monomer to achieve inorganic loadings of 25% by weight (Example 2) and 75% by weight (Example 3). The 75% by weight loaded material was coated on to a polycarbonate substrate rather than an acrylic substrate.

Examples 4 and 5

Example 1 was repeated substituting the organic monomer with a further UV-curable aliphatic urethane acrylate monomer, sold by Akcros Chemicals under product code 260GP25, in appropriate amounts to achieve inorganic loading of 25% (Example 4) and 50% by weight (Example 5). In Example 5, the inorganic sol was aged by heating at 80°C for 5 days, rather than for 24 hours.

The hardness of the coated materials was measured using a scuff test and by the Konig hardness test.

Scuff Test

The scuff test is an in-house method for scouring samples. Two pieces of Scotchbrite® abrasive mat are secured to a metal plate and this arrangement is placed on the bit of a standard upright drill. The samples are fixed at a distance of 70 mm from the drill bit, the Scotchbrite material is rotated at 500 rpm, and contacts the sample over a distance of approximately 60 mm. The samples are scuffed for 10 second bursts, and examined until the first

signs of abrasion are observed. The time taken for this is the measure of scuff resistance.

Coated substrates made in accordance with Examples 1, 3 and 5 were evaluated by the scuff test, and compared with substrates coated with a number of commercially-available silicone hardcoats. The commercially-available silicone hardcoats are available from GE Bayer, and are marketed as: PHC587 - primerless, weatherable grade coating; AS4000 - premium performance, abrasion resistant, weatherable hardcoat; and SHC1200 - optical grade abrasion resistant hardcoat. These were coated onto polycarbonate substrates at thicknesses of between 5 and 10 μm .

The results are summarised in Table 1 below.

Table 1

Coating System	Coating Identity	Substrate material	Primer Required	Curing Temperature	Coating thickness (μm)	Scuff resistance (secs)
Commercially available silicone hardcoats (supplied by GE Bayer)	PHC587	Polycarbonate	No	130°C	5-10	30
	AS4000	Polycarbonate	Yes	130°C	5-10	60
	SHC1200	Polycarbonate	Yes	130°C	5-10	600
Example 1	50% inorganic in 210TP30	Acrylic	No	80°C	50	30
Example 3	75% inorganic in 210TP30	Polycarbonate	No	80°C	50	60
Example 5	50% inorganic in 260GP25	Acrylic	No	80°C	50	580

The results illustrate that the coatings of the invention have similar hardness to, or better hardness than, the PHC587 and AS4000 silicone hardcoats. While the coatings of the invention are not as hard as the SHC1200 silicone hardcoat, with further ageing of the sol it is

believed that coatings can be achieved in accordance with the present invention having superior hardness to this material.

Drawbacks with the commercially-available silicone
5 hardcoats include the fact that they cannot be properly hardened when deposited on acrylic substrates, since they require a curing temperature of around 130°C, which causes acrylic substrates to deform. Furthermore, they can only be coated to thicknesses of up to 10 µm, otherwise cracking
10 occurs. Furthermore, of the three commercially-available silicone hardcoats tested, only PHC587 can be used without first applying a primer coating. In contrast, the coatings according to the present invention do not need a primer.

15 Konig Hardness

The Konig hardness test is a standard method for measuring the deformability of soft plastic coatings. The test uses the damping effect of the coating to slow down a pendulum. The softer the coating the more the fulcrum of
20 the pendulum penetrates and the greater the contact surface area on the fulcrum. This therefore slows the pendulum more quickly. The results are usually presented as number of swings (or time in seconds) for a pendulum set swinging from 6° from the vertical to slow down to achieve only 3°
25 from the vertical.

The results achieved with the coatings of the invention are shown below in Table 2, compared against samples coated solely with organic resin, i.e. 0% inorganic loading.

30

35

Table 2

Resin Type	Inorganic loading (wt%)	Konig Hardness (secs)	
		Polycarbonate substrate.	Acrylic substrate
210TP30	0	73	58
	25	127	112
	50	160	115
260GP25	0	173	145
	25	221	237
	50	228	228

As can be seen from these results, increasing the inorganic (or ceramic) loading level in a given base resin increases the hardness of the resultant coating. As a general rule, as the amount of inorganic in the composite coating increases so does the hardness.

CLAIMS

1. A polymeric sol-gel process for producing a composite material comprising the steps of:

5 (1) initiating polymerisation of inorganic monomers, to form a sol;

(2) forming an homogeneous mixture comprising the sol and organic monomers; and

10 (3) polymerising the organic monomers and taking polymerisation of the inorganic monomers substantially to completion, to form a composite material comprising a mixture of an inorganic polymer and an organic polymer.

2. A process according to claim 1, wherein step (1) comprises initiating hydrolysis of hydrolysable inorganic monomer precursors, and polycondensation of the resulting
15 inorganic monomers, to form a sol.

3. A process according to claim 2, wherein step (1) comprises forming an homogeneous mixture of hydrolysable inorganic monomer precursors, water, and, optionally, a volatile organic solvent.

20 4. A process according to claim 2, wherein step (1) comprises adding water to a solution of hydrolysable inorganic monomer precursors in a volatile organic solvent.

5. A process according to claim 3 or claim 4, wherein the organic solvent, if present, comprises an alcohol.

25 6. A process according to any preceding claim, which comprises, in step (2), adding the organic monomers to the sol, and then initiating polymerisation of the organic monomers prior to taking polymerisation of the inorganic monomers substantially to completion.

30 7. A process according to claim 6, which further comprises ageing the sol prior to addition of the organic monomers.

8. A process according to claim 6 or claim 7, wherein the organic monomers are added to the sol in liquid or solution
35 form.

9. A process according to any preceding claim, which further comprises removing solvent and/or volatile components prior to polymerising the organic monomers.
10. A process according any preceding claim, wherein the
5 organic monomers comprise monomers polymerisable to form a thermoplastic or a thermosetting material.
11. A process according to claim 10, wherein the organic monomers are selected from carbonates, (meth)acrylates, urethanes and terephthalates.
- 10 12. A process according to any preceding claim, wherein the inorganic monomers, are formed by hydrolysis of inorganic monomer precursors comprising inorganic alkoxides, including alkoxides substituted with at least one non-hydrolysable group, and preferably they are formed
15 by hydrolysis of optionally-substituted alkoxysilanes.
13. A process according to any preceding claim, which further comprises use of a crosslinking agent to crosslink between the inorganic and organic polymers, wherein preferably the crosslinking agent is an inorganic alkoxide
20 substituted with a non-hydrolysable organic group, and more preferably is an alkyl-substituted alkoxysilane.
14. A process according to any preceding claim, wherein polymerisation of the organic monomer is initiated by adding a polymerisation initiator prior to step (3).
- 25 15. A process according to any of claims 1 to 13, wherein polymerisation of the organic monomers is initiated by irradiation with UV or IR light, bombardment by electron beams or X-rays, or by heat treatment.
16. A process according to any preceding claim, wherein
30 the organic monomers are present in an amount of 5 to 95%, preferably 50 to 85%, by weight of the total of inorganic monomers and organic monomers.
17. A process according to any preceding claim, which further comprises after step (3) casting, shaping or
35 moulding the material obtained into an article.
18. A composite material obtainable by a process according to any preceding claim.

19. An amorphous composite material which comprises a mixture of an inorganic polymer, derived from the polycondensation of inorganic monomers, and an organic polymer.
- 5 20. A composite material according to claim 19, wherein the inorganic polymer and the organic polymer interpenetrate, preferably on the nanometre scale.
21. A composite material according to claim 19 or claim 20, wherein the inorganic polymer is obtainable by
10 polymerisation of inorganic alkoxides and the organic polymer is a thermoplastic or a thermosetting polymer.
22. A composite material according to any of claims 19 to 21, which is transparent to visible light.
23. An article made by shaping, molding or casting a
15 composite material as defined in any of claims 19 to 22, wherein preferably the article is a window, a windscreen, a protective visor, a lens, an optical filter, or a light casing.
24. An article having a coating comprising a composite
20 material as defined in any of claims 17 to 21, the coating preferably having a thickness of up to 1 mm.
25. An article according to claim 24, which comprises a thermoplastic or a thermosetting material.
26. Use of a composite material as defined in any of
25 claims 18 to 22 as a substitute for glass.
27. Use of a composite material as defined in any of claims 18 to 22, as an adhesive or welding material, or as a sealant.
28. A composition comprising an inorganic sol obtainable
30 by hydrolysis of hydrolysable inorganic monomer precursors, and mixed therewith, organic monomers.
29. A process for providing a protective coating on a substrate, comprising coating on to the substrate a composition as defined in claim 27, and polymerising the
35 inorganic monomers formed on hydrolysis, and polymerising the organic monomers, to form a solid coating.

ABSTRACTCOMPOSITE MATERIALS, THEIR PRODUCTION AND USES

5 A process for producing a composite material comprises the steps of:

 (1) initiating polymerisation of inorganic monomers, to form a sol;

 (2) prior to completing polymerisation of the
10 inorganic monomers, initiating polymerisation of organic monomers homogeneously mixed with the sol; and

 (3) polymerising the organic monomers and taking polymerisation of the inorganic monomers substantially to completion, to form a composite material comprising a
15 mixture of an inorganic polymer and an organic polymer.

 The resulting composite material comprises interpenetrating inorganic and organic polymer networks. It may be used as a protective coating for a wide variety of substrates, or it may be shaped into an article for use
20 in its own right, for instance as a substitute for glass.

